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NOTE

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On the structure and phase transition of lanthanum titanate

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Abstract : This research note reports the structure and phase transition studies of lanthanum titanate ($LaTiO_3$) through XRD pattern, dielectric and electrical conductivity measurements. It has been found that $LaTiO_3$ has orthorhombic unit cell at room temperature and satisfies the criterion put forward by Roth for the Perovskite structure. The phase transition temperature has been found to be (1030 ± 10) K.

Keywords : XRD pattern, transition temperature, Perovskite structure

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Most of the compounds with general formula ABO_3 have perovskite structure with a cubic unit cell. The cation A in this structure is coordinated with twelve oxygen ions and cation B with six oxygen ions. In very early studies, Goldschmidt [1] has put forward a criteria for ideal cubic structure in terms of tolerance factor t which is given by the relation :

$$t = \frac{R_A + R_O}{2(R_B + R_O)}.$$

According to the author and quoted by others [2], the tolerance factor should lie in the range $0.8 \leq t < 0.9$ for ideal perovskite structure. $LaTiO_3$ along with many other lanthanum compounds with general formula ABO_3 satisfy this criteria as evident from Table 1. However, except $LaTiO_3$, all are reported [2] to have orthorhombic unit cell with parameters a_0, b_0 and c_0 as given in Table 1.

Table 1. Ionic radii, tolerance factor (t) and structural parameters of few $LaMO_3$ type compounds with orthorhombic unit cell. Radii of La^{3+} and O^{2-} are 0.1061 nm and 0.1400 nm respectively

$LaMO_3$ with M =	Radius of M^{3+} ions (nm)	Tolerance factor (t)	Unit cell parameter			Reference
			a_0 (nm)	b_0 (nm)	c_0 (nm)	
Mn	0 066	0 845	0.5536	0.5726	0 7697	3
Fe	0 067	0.841	0 5556	0 5565	0.7862	2
Cr	0.069	0 833	0.5477	0.5515	0.7755	2
Ti	0 070	0 823	0 5570	0 5796	0.7680	PS
Sc	0.081	0.787	0 5678	0 5787	0.8098	2

PS = Present study

$LaTiO_3$ is reported [4,5] to have cubic structure with a = 0.392 nm. It is evident from this table that lower limit of tolerance factor 0.8 is not appropriate for ideal perovskite structure. It is worth mentioning at this stage that the criteria for different types of perovskite structure has been dealt in detail by Roth [6] and a summarized result of the same is presented by Glasso [2]. According to criteria presented in a figure by the authors [2,6], $LaTiO_3$ should have orthorhombic unit cell at room temperature. To resolve this anamoly between the reported structure and criteria put by Roth [6], we have prepared and studied the structure and phase transition of $LaTiO_3$ by dielectric constant and electrical conductivity measurement and the results are presented in this note. The starting materials for the preparation of $LaTiO_3$ were La_2O_3 (with stated purity of 99.99% from Rare and Research Chemical, Bombay, India) and TiO_2 (stated purity of 99.9% from the same firm). The two oxides were dried for four hours at ≃450 K. Then they are mixed in stoichiometric amount and heated in silica crucible in air at about 1200 K for 48 hours with one intermediate grinding. The compound is formed according to the following solid state reaction :

$$La_2O_3 + 2TiO_2 \xrightarrow{1200\ K} 2LaTiO_3 + O\uparrow.$$

The loss of the sample after heating was recorded. The loss was well within the range expected from above equation. The X-ray diffraction (XRD) pattern of prepared compound has been recorded using CuK_α radiation (λ = 0.15405 nm) and diffraction peaks were analyzed using standard procedure. All the peaks could be assigned by proper h, k, l values (Table 2) as per relation :

$$d_{hkl} = b_0\left[(h/a)^2 + k^2 + (l/c)^2\right]^{-1/2},$$

where a_0, b_0 and c_0 are lattice parameters and $a = a_0/b_0$ and $c = c_0/b_0$. The analysis shows that the compound has orthorhombic unit cell with a_0 = 0.5570 nm, b_0 = 0.5796 nm and c_0 = 0.7680 nm.

It is normal tendency of the less symmetrical structure to undergo phase transition and yield more symmetrical structure at higher temperatures. Since $LaTiO_3$ is orthorhombic

Table 2. Experimental and calculated values of d_{hkl} and the h, k, l values for intense peaks in XRD pattern.

d_{hkl}				
Experimental (nm)	Theoretical (nm)	h	k	l
0.2786	0.2785	2	0	0
0.2440	0.2438	1	2	1
0 2257	0 2255	2	0	2
0.1916	0 1920	0	0	4
0 1812	0.1815	1	2	3
0 1763	0 1763	2	1	0
0 1612	0 1606	3	1	2
0 1449	0 1449	0	4	0
0 1356	0 1356	0	4	2
0 1340	0 1337	3	3	0

at room temperature, it is expected to go to tetragonal or cubic structure at higher temperatures. If it happens, then we can expect sharp anomalies at transition temperature in both dielectric constant and electrical conductivity. To see this, we prepared pressed pellets of powdered $LaTiO_3$, annealed it around 1000 K for few hours and measured its density. The density of pressed pellets was about 80 percent of the evaluated density using structure data. Using painted silver and hard platinum electrodes and two-electrode method, the capacitance and resistance of the pellets were measured at different temperatures employing LCR Q-meter (Aplab, India). Using these data and dimensions of the pellet, dielectric constant (K) and electrical conductivity (σ) were calculated at different temperatures. The results at higher temperatures are presented in Figures 1 and 2. It is seen

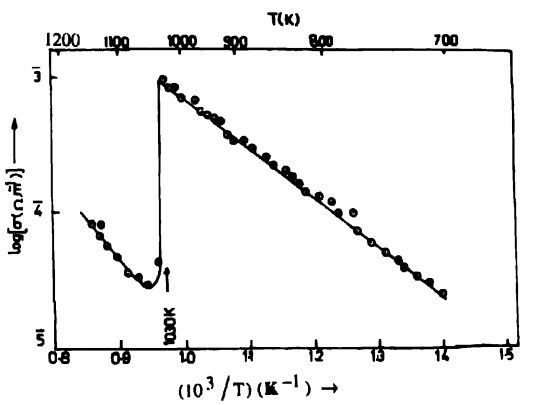

Figure 1. Variation of logarithm of electrical conductivity (log σ) *vs* inverse of absolute temperature (T^{-1}) for pressed pellet of $LaTiO_3$.

from Figure 1 that σ drops by a factor of 30 around 1030 K and K *vs* T plot shows a well-defined peak at the same temperature. These anamolies are probably due to phase transition

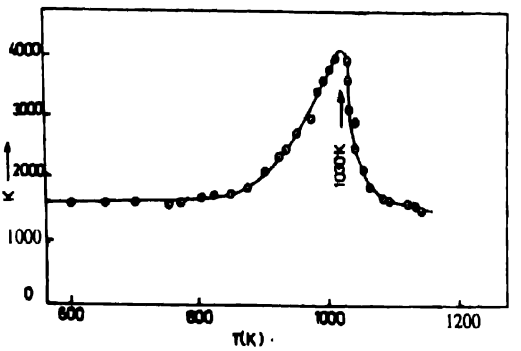

Figure 2. Variation of dielectric constant (K) *vs* absolute temperature (T) for pressed pellet of $LaTiO_3$

of $LaTiO_3$ around (1030 ± 10) K. The detail analysis of σ and K data will be presented elsewhere.

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